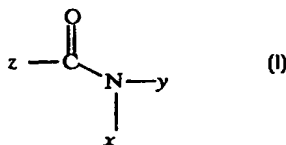


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/16372 <b>(22) International Filing Date:</b> 20 July 1999 (20.07.99)  <b>(30) Priority Data:</b> 60/093,458 20 July 1998 (20.07.98) US  <b>(71) Applicant:</b> KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).  <b>(72) Inventors:</b> NOHR, Ronald, Sinclair; 8955 Nesbit Lakes Drive, Alpharetta, GA 30202 (US). MCDONALD, John, Gavin; 1472 Knollwood Terrace, Decatur, GA 30033 (US).  <b>(74) Agents:</b> WITHERS, James, D.; Jones & Askew, LLP, 2400 Monarch Tower, 3424 Peachtree Road, Atlanta, GA 30326 (US) et al.		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** IMPROVED INK JET INK COMPOSITIONS**(57) Abstract**

The present invention is directed to compositions containing a colorant and at least one water-soluble solvent, wherein the water-soluble solvent is a compound having general formula (I): wherein x is hydrogen or an alkyl having from 1 to 6 carbons; y is an alkyl having from 1 to 6 carbons; and z is an alkyl having from 1 to 6 carbons.

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## IMPROVED INK JET INK COMPOSITIONS

### Technical Field

The present invention relates to colorant compositions, particularly to ink jet ink compositions.

15

### Background of the Invention

20

The use of pyrrolidone and glycols as suitable "solvents" in colorant compositions is well known in the art of ink jet printing. For example, U.S. Patent No. 5,108,503 to Hindagolla et al., assigned to Hewlett-Packard Company, Palo Alto, CA, disclosed ink jet ink compositions containing one or more solvents in the form of pyrrolidones. Other ink compositions containing glycols as suitable solvents are disclosed in numerous patents including, but not limited to,

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U.S. Patents Nos. 3,705,043; 4,381,946; 4,421,559; 4,853,037; 4,957,533; 4,973,499; 5,196,057; 5,207,824; 5,431,724; 5,560,771; and 5,624,484.

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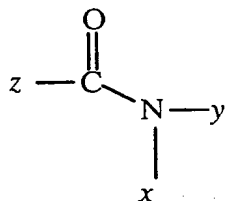
The above-mentioned ink compositions, containing one or more pyrrolidone and/or glycols, result in a hazy or dull color when applied to a number of ink-receiving substrates. Further, the above-described ink compositions possess an undesirable degree of tackiness when applied to a number of ink-receiving substrates. While the above-described ink compositions have a number of desirable properties, such as

minimal spreading, smear resistance and waterfastness, the ink compositions still possess many shortcomings.

What is needed in the art is an ink jet ink composition which may be applied to an ink-receiving substrate without resulting in a hazy appearance or a tacky feel.

### Summary of the Invention

The present invention is directed to compositions containing a colorant and at least one water-soluble compound having the following general formula:



wherein  $x$  is hydrogen or an alkyl having from approximately 1 to 6 carbons;  $y$  is an alkyl having from approximately 1 to 6 carbons; and  $z$  is an alkyl having from approximately 1 to 6 carbons. The presence of the water-soluble compound results in an improved composition with minimal haziness and tackiness. In one embodiment of the present invention, the composition comprises an ink jet ink composition. Other compatible components may be added to the mixture to produce a composition having desired properties, such as lightfastness, waterfastness, pH, etc.

The present invention is also directed to ink-receiving substrates having the above-described composition thereon. Suitable ink-receiving substrates include substrates such as paper, wood, fabrics and films. The present invention is further directed to a method of printing an ink composition onto an ink-receiving substrate.

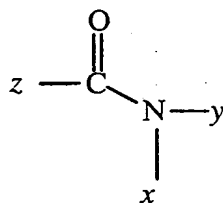
The present invention is also directed to a method of making a composition comprising a colorant and at least one water-soluble compound as described above. At least one

water-soluble compound is incorporated into a mixture containing a colorant. The present invention is also directed to an ink jet ink cartridge containing the above-described composition.

5        These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

### 10        Detailed Description of the Invention

The compositions of the present invention contain a colorant and at least one water-soluble compound having the following general formula:



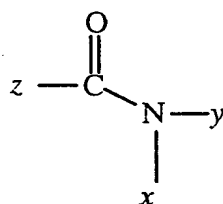
15        wherein  $x$  is hydrogen or an alkyl having from approximately 1 to 6 carbons;  $y$  is an alkyl having from approximately 1 to 6 carbons; and  $z$  is an alkyl having from  
20        approximately 1 to 6 carbons. The compositions possess waterfastness and smear resistance similar to or superior to colorant compositions of the prior art, but also have minimal haziness and tackiness regardless of the ink-receiving substrate. The present invention is also directed to ink-receiving substrates having the above-described composition thereon.

25        As used herein, the term "composition" and such variations as "colored composition" are used herein to mean a colorant and one or more water-soluble compounds described above. The composition may optionally include  
30        other compatible components.

As used herein, the term "colorant" is meant to include, without limitation, any material which typically will be an organic material, such as an organic colorant or dye. The term is meant to include a single material or a mixture of two or more materials.

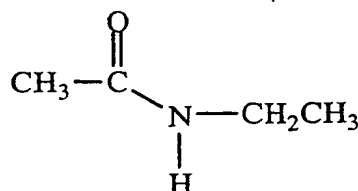
The term "thereon" is used herein to mean thereon or therein. For example, the present invention includes a substrate having a colored composition thereon. According to the definition of "thereon" the colored composition may be present on the substrate or it may be in the substrate.

The water-soluble compounds used in the compositions of the present invention have the following general formula:

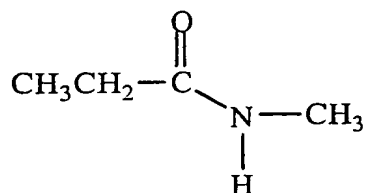


wherein  $x$  is hydrogen or an alkyl having from 1 to 6 carbons;  $y$  is an alkyl having from 1 to 6 carbons; and  $z$  is an alkyl having from 1 to 6 carbons. The substituents  $x$ ,  $y$  and  $z$  are selected to result in a compound which is water soluble. In some desired embodiments,  $x$  is hydrogen;  $y$  is an alkyl having from 1 to 3 carbons; and  $z$  is an alkyl having from 1 to 3 carbons. In more desired embodiments,  $x$  is hydrogen;  $y$  is an alkyl having from 1 to 2 carbons; and  $z$  is an alkyl having from 1 to 2 carbons.

In one embodiment of the present invention, the water-soluble compound comprises



In a further embodiment, the water-soluble compound comprises



5

The water-soluble compound may be present in the composition in any amount as long as the composition is suitable for use. For example, when the composition is an ink jet ink composition, the amount of water-soluble compound may need to be less than for another type of coating. Desirably, the amount of water-soluble compound in the composition of the present invention is up to about 25 weight percent based on the total weight of the composition. In some desired embodiments of the present invention, the water-soluble compound is present in an amount of about 2 to 25 weight percent based on the total weight of the composition. In more desired embodiments of the present invention, the water-soluble compound is present in an amount of about 6 to 10 weight percent based on the total weight of the composition.

20

The compositions of the present invention may include any colorant known in the art. Suitable colorants include, but are not limited to, dyes and pigments. Desirably, the colorant is an organic dye. Organic dye classes include, by way of illustration only, triarylmethyl dyes, such as Malachite Green Carbinol base {4-(dimethylamino)-a-[4-(dimethylamino)phenyl]-a-phenyl-benzene-methanol}, Malachite Green Carbinol hydrochloride {N-4-[[4-(dimethylamino)phenyl]phenyl-methylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[p-(dimethylamino)phenyl]phenylmethylium chloride},

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and Malachite Green oxalate {N-4-[[4-(dimethylamino)-phenyl]-phenylmethylen]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[*p*-(dimethylamino)-phenyl]phenylmethylium oxalate}; monoazo dyes, such as  
 5 Cyanine Black, Chrysoidine [Basic Orange 2; 4-(phenylazo)-1,3-benzenediamine monohydrochloride], Victoria Pure Blue BO, Victoria Pure Blue B, basic fuschin and  $\beta$ -Naphthol Orange; thiazine dyes, such as Methylene Green, zinc  
 10 chloride double salt [3,7-bis(dimethylamino)-6-nitrophenothiazin-5-ium chloride, zinc chloride double salt]; oxazine dyes, such as Lumichrome (7,8-dimethylalloxazine); naphthalimide dyes, such as Lucifer Yellow CH {6-amino-2-[(hydrazino-carbonyl)amino]-2,3-dihydro-1,3-dioxo-1H-  
 15 benz[de]iso-quinoline-5,8-disulfonic acid dilithium salt}; azine dyes, such as Janus Green B {3-(diethylamino)-7-[[4-(dimethyl-amino)phenyl]azo]-5-phenylphenazinium  
 chloride}; cyanine dyes, such as Indocyanine Green {Cardio-Green or Fox Green; 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-  
 20 1,1-dimethyl-3-(4-sulfobutyl)-1H-benz[e]indolium hydroxide inner salt sodium salt}; indigo dyes, such as Indigo {Indigo Blue or Vat Blue 1; 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one}; coumarin dyes, such as 7-hydroxy-4-methyl-coumarin (4-methylumbelliferone);  
 25 benzimidazole dyes, such as Hoechst 33258 [bisbenzimidazole or 2-(4-hydroxyphenyl)-5-(4-methyl-1-piperazinyl)-2,5-bi-1H-benzimidazole trihydro-chloride pentahydrate]; paraquinoidal dyes, such as Hematoxylin {Natural Black 1; 7,11b-dihydrobenz[b]-indeno[1,2-d]pyran-3,4,6a,9,10(6H)-  
 30 pentol}; fluorescein dyes, such as Fluoresceinamine (5-aminofluorescein); diazonium salt dyes, such as Diazo Red RC (Azoic Diazo No. 10 or Fast Red RC salt; 2-methoxy-5-chlorobenzenediazonium chloride, zinc chloride double salt); azoic diazo dyes, such as Fast Blue BB salt (Azoic Diazo No.  
 35 20; 4-benzoylamino-2,5-diethoxy-benzene diazonium

chloride, zinc chloride double salt); phenylenediamine dyes, such as Disperse Yellow 9 [N-(2,4-dinitrophenyl)-1,4-phenylenediamine or Solvent Orange 53]; diazo dyes, such as Disperse Orange 13 [Solvent Orange 52; 1-phenylazo-4-(4-hydroxyphenylazo)naphthalene]; anthra-quinone dyes, such as Disperse Blue 3 [Celliton Fast Blue FFR; 1-methylamino-4-(2-hydroxyethylamino)-9,10-anthraquinone], Disperse Blue 14 [Celliton Fast Blue B; 1,4-bis(methylamino)-9,10-anthraquinone], and Alizarin Blue Black B (Mordant Black 13); trisazo dyes, such as Direct Blue 71 (Benzo Light Blue FFL or Sirius Light Blue BRR; 3-[(4-[(4-[(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo]-6-sulfo-1-naphthalenyl)-azo]-1-naphthalenyl)azo]-1,5-naphthalenedisulfonic acid tetrasodium salt}; xanthene dyes, such as 2,7-dichloro-fluorescein; proflavine dyes, such as 3,6-diaminoacridine hemisulfate (Proflavine); sulfonaphthalein dyes, such as Cresol Red (o-cresolsulfonaphthalein); phthalocyanine dyes, such as Copper Phthalocyanine (Pigment Blue 15; (SP-4-1)-[29H,31H-phthalocyanato(2-)-N<sup>29</sup>,N<sup>30</sup>,N<sup>31</sup>,N<sup>32</sup>]copper); carotenoid dyes, such as trans- $\beta$ -carotene (Food Orange 5); carminic acid dyes, such as Carmine, the aluminum or calcium-aluminum lake of carminic acid (7-a-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracene-carboxylic acid); azure dyes, such as Azure A [3-amino-7-(dimethylamino)phenothiazin-5-ium chloride or 7-(dimethyl-amino)-3-imino-3H-phenothiazine hydrochloride]; and acridine dyes, such as Acridine Orange [Basic Orange 14; 3,8-bis(dimethylamino)acridine hydrochloride, zinc chloride double salt] and Acriflavine (Acriflavine neutral; 3,6-diamino-10-methylacridinium chloride mixture with 3,6-acridine-diamine).

The colorant compositions of the present invention may contain a number of additional components depending on the desired properties of the resulting composition. To

improve lightfastness, one or more colorant stabilizers may be added to the composition. In one embodiment of the present invention, a colorant stabilizer in the form of a porphine is added to the colorant composition. Suitable porphines include, but are not limited to, porphines such as those disclosed in U.S. Patent No. 5,782,963 and U.S. Patent Applications Serial Nos. 08/788,863 and 08/843,410, all of which are assigned to Kimberly Clark Worldwide, Inc.

In addition to the colorant and optional colorant stabilizer, the colored compositions of the present invention may contain additional components, depending upon the application for which it is intended. Examples of such additional components include, but are not limited to, buffering agents; charge carriers; stabilizers against thermal oxidation; viscoelastic properties modifiers; cross-linking agents; plasticizers; charge control additives such as a quaternary ammonium salt; flow control additives such as hydrophobic silica, zinc stearate, calcium stearate, lithium stearate, polyvinylstearate, and polyethylene powders; fillers such as calcium carbonate, clay and talc; surfactants; chelating agents; and TINUVIN<sup>®</sup> compounds; among other additives used by those having ordinary skill in the art. Charge carriers are well known to those having ordinary skill in the art and typically are polymer-coated metal particles. Desirable surfactants include, but are not limited to, C<sub>12</sub> to C<sub>18</sub> surfactants such as cetyl trimethyl ammonium chloride and carboxymethylamylose. TINUVIN<sup>®</sup> compounds are a class of compounds produced by Ciba-Geigy Corporation, which includes benzophenones, benzotriazoles and hindered amines. Desirable TINUVIN<sup>®</sup> compounds include, but are not limited to, 2-(2'-hydroxy-3'-*sec*-butyl-5'-*tert*-butylphenyl)-benzo-triazole, poly-(N-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate and 2-(2'-hydroxy-3',5'-*diter*tbutylphenyl)-5-chloro-benzotriazole. The identities and amounts of such

additional components in the colored composition are well known to one of ordinary skill in the art.

Suitable solvents include, but are not limited to, amides, such as N,N-dimethylformamide; sulfoxides, such as dimethylsulfoxide; ketones, such as acetone, methyl ethyl ketone, and methyl butyl ketone; aliphatic and aromatic hydrocarbons, such as hexane, octane, benzene, toluene, and the xylenes; esters, such as ethyl acetate; water; and the like. Desirably, the solvent is water.

The present invention is also directed to ink-receiving substrates having the above-described composition thereon. The substrates to which the colorant and water-soluble compounds are applied include, but are not limited to, paper, wood, a wood product or composite, woven fabric, nonwoven fabric, textile, plastic, glass, metal, or any other substrate that would benefit from having a colorant thereon. Examples of suitable substrates are disclosed in U.S. Patent Application Serial No. 08/843,410, assigned to Kimberly Clark Worldwide, Inc., the entire content of which is hereby incorporated by reference.

The present invention is also directed to a method of making a composition comprising a colorant and at least one water-soluble compound as described above. At least one water-soluble compound is incorporated into a mixture containing a colorant. The method of combining the colorant and water-soluble compound may be any method known to those of ordinary skill in the art.

The present invention is also directed to an ink jet ink cartridge containing the above-described composition.

The present invention is further directed to a method of printing an ink composition onto an ink-receiving substrate. In one method of printing of the present invention, an ink composition comprising a colorant and at least one water-soluble compound is ejected from an ink jet head onto an ink-receiving surface.

5 The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or the scope of the present invention. In the examples, all parts are by weight, unless stated otherwise.

### EXAMPLE 1

#### *Preparation of Magenta Ink*

10 A magenta ink was prepared using the following components, given in weight percent:

DI Water	82.76
NaOH (0.5 N solution)	4.00
CuTPPS <sub>4</sub>	0.50
EDTA	0.10
EuNO <sub>3</sub>	0.05
N-methylpropionamide	8.00
GIV-GUARD® DNX (50 wt% solution)	0.40
COBRATEC® 99	0.10
Reactive Red 187 (27 wt% solution)	2.89
Acid Red 52	1.20

15 The resulting ink composition was applied to an ink-receiving substrate as described in pending U.S. patent application serial no. 09/058,385, entitled "Improved Substrate and Colorant Stabilizers", assigned to Kimberly Clark Worldwide, Inc. The applied ink composition was free of haze and tackiness.

## EXAMPLE 2

*Preparation of Magenta Inks*

Two additional magenta ink compositions were prepared using the same components as in Example 1 above except the amount of N-methylpropionamide was 6.0 and 10.0 weight percent respectively.

The resulting ink compositions were applied to ink-receiving substrates as in Example 1. The applied ink compositions were free of haze and tackiness.

## EXAMPLE 3

*Preparation of Cyan Ink*

A cyan ink was prepared using the following components, given in weight percent:

DI Water	69.80
NaOH (0.5 N solution)	3.20
N-methylpropionamide	8.00
GIV-GUARD® DNX (50 wt% solution)	0.40
COBRATEC® 99	0.10
Project Cyan	18.50

The resulting ink composition was applied to an ink-receiving substrate as in Example 1. The applied ink composition was free of haze and tackiness.

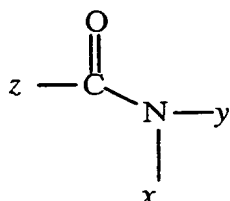
While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these

embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

## Claims

What is claimed is:

5 1. A composition containing a colorant and at least one water-soluble compound having the following general formula:



10 wherein  $x$  is hydrogen or an alkyl having from 1 to 6 carbons;  $y$  is an alkyl having from 1 to 6 carbons; and  $z$  is an alkyl having from 1 to 6 carbons.

2. The composition of Claim 1, wherein the composition is an ink jet ink composition.

15 3. The composition of Claim 2, wherein the water-soluble compound is present in an amount of up to about 25 weight percent based on the total weight of the composition.

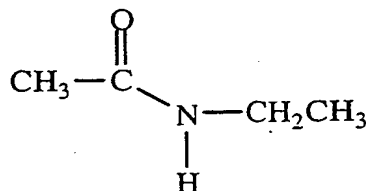
20 4. The composition of Claim 3, wherein the water-soluble compound is present in an amount of about 6 to 10 weight percent based on the total weight of the composition.

25 5. The composition of Claim 3, wherein the composition comprises:

- 30 (a) from about 2 to about 25 weight percent of the water-soluble compound;  
(b) from about 1 to about 10 weight percent colorant; and  
(c) the balance water.

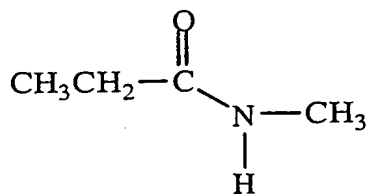
6. The composition of Claim 1, wherein the water-soluble compound comprises

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7. The composition of Claim 1, wherein the water-soluble compound comprises

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8. The composition of Claim 1, further comprising at least one colorant stabilizer.

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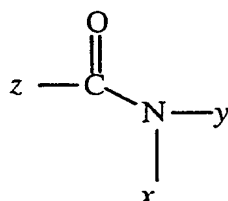
9. The composition of Claim 8, wherein the colorant stabilizer comprises a porphine.

10. A substrate having the composition of Claim 1 thereon.

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11. A method of making a composition comprising:  
combining a colorant and at least one water-  
soluble compound to form a mixture, wherein the one  
water-soluble compound has the following general formula:



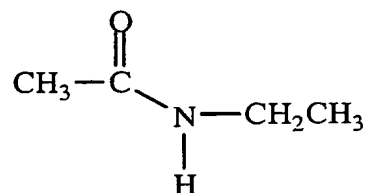
wherein  $x$  is hydrogen or an alkyl having from 1 to 6  
carbons;  $y$  is an alkyl having from 1 to 6 carbons; and  $z$  is an  
alkyl having from 1 to 6 carbons.

12. The method of Claim 11, wherein the  
composition is an ink jet ink composition.

13. The method of Claim 12, wherein the water-  
soluble compound is present in an amount of up to about 25  
weight percent based on the total weight of the  
composition.

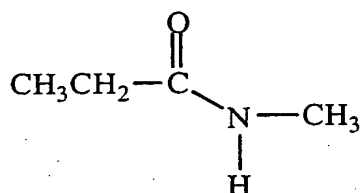
14. The method of Claim 13, wherein the water-  
soluble compound is present in an amount of about 6 to 10  
weight percent based on the total weight of the  
composition.

15. The method of Claim 11, wherein the water-soluble compound comprises



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16. The method of Claim 11, wherein the water-soluble compound comprises

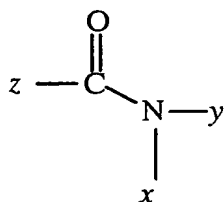


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17. An ink jet ink cartridge containing the composition of Claim 1.

18. A method of printing an ink composition onto a substrate comprising:

5 ejecting an ink composition from an ink jet cartridge onto a substrate; wherein the ink composition comprises a colorant and at least one water-soluble compound, wherein the one water-soluble compound has the following general formula:



10 wherein  $x$  is hydrogen or an alkyl having from 1 to 6 carbons;  $y$  is an alkyl having from 1 to 6 carbons; and  $z$  is an alkyl having from 1 to 6 carbons.

## INTERNATIONAL SEARCH REPORT

Intern .al Application No

PCT/US 99/16372

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 173 112 A (MATRICK HOWARD ET AL) 22 December 1992 (1992-12-22) column 2, line 40-60 column 4, line 47-68 column 6, line 50-54 column 9, line 15-20 ---	1-7, 10-18
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 019 (C-090), 3 February 1982 (1982-02-03) & JP 56 143274 A (CANON INC), 7 November 1981 (1981-11-07) abstract --- -/-	1-5,7, 10-14, 16-18

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

20 October 1999

Date of mailing of the international search report

28/10/1999

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Miller, A

# INTERNATIONAL SEARCH REPORT

Inter:      nal Application No  
PCT/US 99/16372

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PATENT ABSTRACTS OF JAPAN vol. 013, no. 134 (C-581), 4 April 1989 (1989-04-04) &amp; JP 63 297477 A (FUJI PHOTO FILM CO LTD), 5 December 1988 (1988-12-05) abstract</p> <p>-----</p>	<p>1,2,6,7, 10-12, 15-17</p>

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Information on patent family members

International Application No

PCT/US 99/16372

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JP 56143274 A	07-11-1981	JP 1006236 B JP 1526778 C	02-02-1989 30-10-1989
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